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## Sequestering Agents for Metal Immobilization - Application to the Development of Active Caps in Fresh and Salt Water Sediments

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**ABSTRACT:** This research evaluated the removal of inorganic contaminants by a variety of amendments and mixtures of amendments in fresh and salt water. A series of removal and retention batch experiments was conducted to identify the best treatment for metal removal. Metal removal by the amendments was evaluated by calculating the partition coefficient and percent removal. Retention of metals by the amendments was evaluated in retention (desorption) studies in which residue from the removal studies was extracted with 1 M MgCl<sub>2</sub> solution. The results indicated that phosphate amendments, some organoclays (e.g., OCB-750), and the biopolymer, chitosan, are very effective in removal and retention of metals in both fresh and salt water. These amendments are being evaluated further as components in the development of active caps for sediment remediation.

### INTRODUCTION

In contrast to passive capping, active or reactive capping involves the use of capping materials that react with sediment contaminants to reduce their toxicity or bioavailability. Active capping is a less mature technology that holds great potential for a more permanent solution that avoids residual risks resulting from contaminant migration through the cap or breaching of the cap. Existing active caps often require a layer of armoring material to protect them from physical disturbance in dynamic aquatic environments. Apart from the type of amendments to be used in active capping, little is known regarding amendment applications techniques, application rates, and amendment combinations that will maximize immobilization of contaminants.

In this study phosphates, organoclays, aquablok, zeolites, and biopolymers were evaluated for possible incorporation into active caps for the remediation of contaminated sediments. The main source of phosphates is rock phosphate containing the mineral apatite (calcium phosphate). Apatite is a common surface and subsurface amendment (Knox et al., 2003, 2006) that effectively immobilizes Pb and other constituents (e.g., Cd, Ni, Zn, and U) in contaminated sediments (Knox et al., 2003 and 2006; Ma et al., 1997), thus offering an economical and simple treatment method. Calcium phytate removes contaminants in the same manner as apatite minerals. Recent studies have suggested that phytate (IP6) can be applied in a soluble form for delivery to remote contaminated sediments, where it undergoes various reactions that eventually result in the precipitation of the contaminant metals (Nash et al., 1998).

Organoclays consist of bentonite that is modified with quaternary amines. Organoclays are particularly effective at removing non-polar pollutants such as oil, polychlorinated biphenols, chlorinated solvents, and polycyclic aromatic hydrocarbons (Alther 2002, Xu et al. 1997). Organoclays may be used in combination with phytate or other amendments to stabilize both organic and inorganic contaminants.

The zeolites are framework silicates consisting of interlocking tetrahedrons of  $\text{SiO}_4$  and  $\text{AlO}_4$ . Zeolites have large vacant spaces or cages in their structures that allow space for cations and even relatively large molecules and cation groups such as water, ammonia, carbonate ions and nitrate ions. Zeolites have many useful purposes - ion exchange, filtering, odor removal, and chemical sieve. Many researchers have reported effective metal removal by zeolite. For example, a study by Leppert (1990) reported that zeolite, especially clinoptilolite, demonstrates strong affinity for Pb, Cr, and Cd.

Biopolymers are high-molecular weight compounds with repeated sequences that may become multiple reactive sites with high opportunity for chemical interaction with other compounds. Depending on their functional groups, biopolymers can bind metals or soil particles, and can form interpenetrating cross-linking networks with other polymers (Berkeley, 1979; Yang and Zall, 1984).

The objective of this study was to evaluate the ability of sequestering materials (in different combinations) to remove and retain a broad range of contaminants from fresh and salt water under controlled laboratory conditions.

## **MATERIALS AND METHODS**

Removal and retention of As, Cd, Cr, Co, Cu, Pb, Ni, Se, and Zn in fresh water was evaluated for 12 amendments. The 12 amendments included two rock phosphates (from Tennessee and North Carolina), biological apatite (ground fish bones), calcium phytate, three organoclays from Biomin, Inc. (Clayfloc TM 200, 202, and 750), two types of aquablok from AquaBlok, Ltd. (one with a clay coating and one with a zero valent iron coating), two types of zeolite (phyllophite and clinoptilolite), a biopolymer (chitosan), and sand (as a control). The experiment was conducted in 50 mL centrifuge tubes for a period of one week. Each treatment had three replicates: two for metal analysis by inductively coupled plasma-mass spectrometer (ICP-MS) and a third for pH measurements. The spike solution used in the experiment was obtained from Inorganic Ventures, Lakewood, NJ. The metal concentration in the spike solution was  $1 \text{ mg L}^{-1}$  of As, Cd, Cr, Co, Cu, Pb, Ni, Se, and Zn. Suspensions composed of 0.2 g of solid (the sequestering agent) and 15 mL of spike solution were shaken for one week, phase separated by centrifugation, and then analyzed for metal content by ICP-MS and pH. There were 12 treatments with individual amendments and 6 with mixtures of amendments. The mixtures were tested to determine if their removal effectiveness was greater than that of individual amendments.

The data obtained in this experiment were used to calculate percent removal (sorption) and partition coefficient ( $K_d$ ) values, defined as the ratio of the concentration of solute sorbed to the solid divided by its concentration in solution. Presenting the sorption data as percent removal instead of concentrations ( $\text{mg L}^{-1}$ ) facilitated comparisons among amendments. The  $K_d$  ( $\text{mL/g}$ ) was calculated using Eq. (1) (American Society for Testing and Materials, 1993):

$$K_d = V_{\text{spike}} (C_{\text{spike}} - C_{\text{final}}) / C_{\text{final}} \times M_{\text{Mineral}} \quad (1)$$

where  $C_{\text{spike}}$  is the metal concentration in the spike solution before the addition of the amendment (mg/L),  $C_{\text{final}}$  is the metal concentration in the solution after contact with the amendment (mg/L),  $M_{\text{mineral}}$  is the amendment mass (g), and  $V_{\text{spike}}$  is the volume of the spike solution (mL).

The retention study was run on the residue from the sorption study. The residue was washed twice with deionized water and extracted with 1 M  $\text{MgCl}_2$  to determine the readily available pool of sorbed metals. After 1 hour, the samples were centrifuged and the supernatant decanted. The extract was analyzed for metals by ICP-MS. The desorption and sorption data were used to calculate percentage retention on each tested amendment using equation 2:

$$\% \text{ retention} = [(C_{\text{adsorbed}} - C_{\text{desorbed}}) / C_{\text{spike}}] \times 100 \quad (2)$$

where  $C_{\text{desorbed}}$  is the concentration of metal desorbed at the end of the desorption experiment,  $C_{\text{adsorbed}}$  is the concentration of metal adsorbed at the end of the adsorption experiment, and  $C_{\text{spike}}$  is the concentration of metal in the spike solution.

The removal and retention experiments in salt water were conducted as described for fresh water, except the spike solution was made from artificial ocean water (salinity 3.5%) and there were fewer treatments. The following amendments were evaluated: sand (as a control), rock phosphate from Tennessee, North Carolina apatite, calcium phytate, organoclay (OCB-750), two aquablok materials, zeolite (clinoptilolite), chitosan, and a mixture of North Carolina apatite and chitosan.

## RESULTS AND DISCUSSION

In this study  $K_d$  values were determined from sorption experiments for nine elements that are typical in contaminated sediments (As, Cd, Cr, Co, Cu, Pb, Ni, Se, and Zn). It is important to note that the results from laboratory batch sorption tests generally allow no distinction to be made on how the sorbate (i.e., contaminant) is associated with the sorbent (i.e., sediment or sequestering agent). The sorbate may be adsorbed by ion exchange, chemisorption, bound to complexes that are themselves sorbed on the solid, and/or precipitated.

The  $K_d$  values in fresh water were highly variable, differing by an order of magnitude (Figure. 1), but were useful in identifying effective amendments. Phosphates (especially rock phosphate from North Carolina and calcium phytate), organoclay (OCB-750), and biopolymer (BPC) had relatively high  $K_d$  values for Cd, Cr, Cu, Pb, Ni, and Zn (Figure 1). Only OCB-750 and the mixture of NCA and OCB-750 produced relatively high  $K_d$  values for As and Se. Even though OCB-750 had very high  $K_d$  values for all metals, it may not be effective by itself in sediment caps due to high alkalinity, light weight, and cost. Therefore, mixtures such as OCB-750 and apatite might be promising and will be evaluated further.

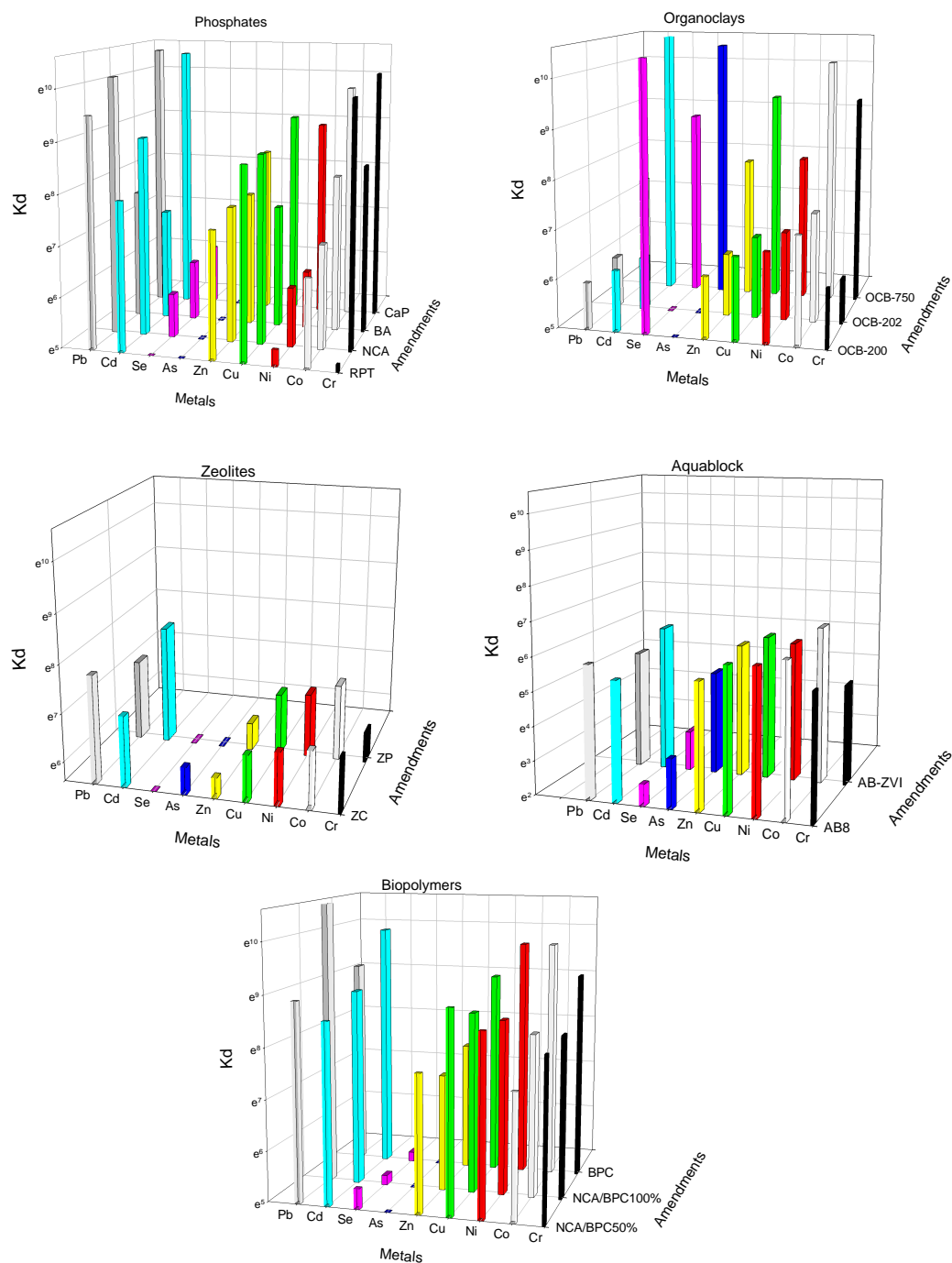


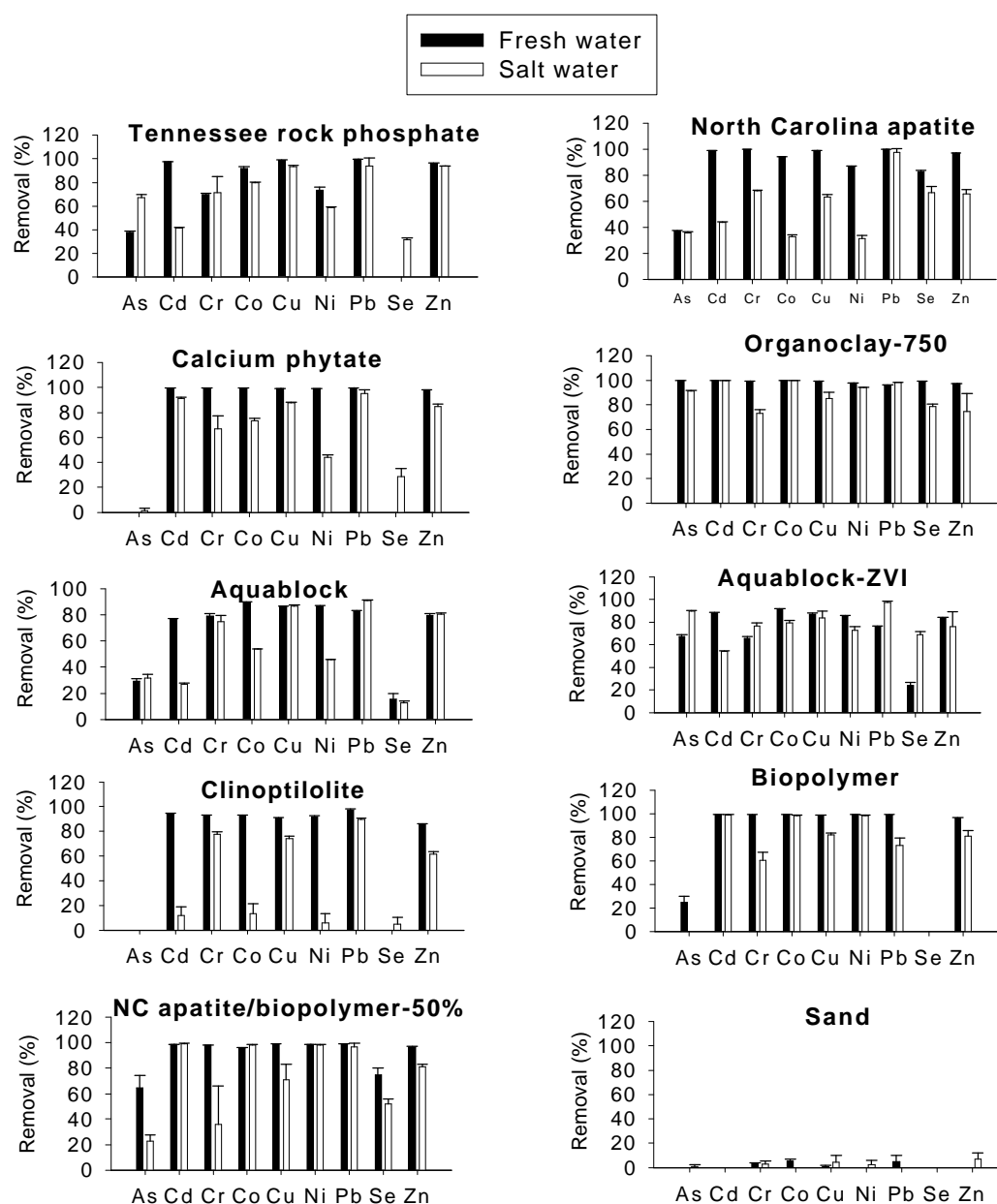
Figure 1. Partition coefficients ( $K_d$ ) for As, Cd, Cr, Co, Cu, Ni, Pb, Se, and Zn in fresh water; RPT – rock phosphate from Tennessee, NCA- North Carolina apatite, BA- biological apatite, CaP – calcium phytate, OCB – organoclays from Biomin Inc., AB8 – aquablok with clay coating, AB-ZVI aquablok with zero valent iron, ZC – clinoptilolite zeolite, ZP – phillipsite zeolite, BPC – chitosan biopolymer.

The removal (sorption) of Cd, Co, Cr, Cu, Pb, and Zn from spike solutions in fresh water was very high for almost all tested amendments (Figure 2), but removal of As and Se was only effective for OCB-750, AB-ZVI, and mixtures of NCA with OCB-750 or BPC. Removal in salt water (3.5% salinity, room temperature, alkaline pH) was very high for most metals, especially Cr, Cu, Pb, and Zn (Figure 2). However, the removal of Cd, Co, Ni, and some other elements by phosphates in salt water was lower than in fresh water (Figure 2). Clinoptilolite zeolite effectively removed only Cr, Cu, Pb, and Zn in both fresh and salt water (Figure 2). Other researchers have reported that sorption by clinoptilolite is not affected by increased  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$  in solution (Ponizovsky and Tsadilas, 2003); however, in this study sorption by clinoptilolite was substantially lower in salt water than in fresh water (Figure 2). A study by Leppert (1990) reported that zeolite, especially clinoptilolite, demonstrates strong affinity for Pb, Cr and Cd.

Organoclay (OCB-750) removed the tested metals about equally from metal spiked fresh and salt water (Figure 2), with lower performance only for Se in fresh water. The aquablock amendment with zero valent iron coating removed As and Se more efficiently in salt water than fresh water (Figure 2). Chitosan, the only biopolymer tested so far, was very promising as a stand-alone amendment and when mixed with phosphate amendments (Figure 2). Chitosan can be produced chemically from chitin and is found naturally in some fungal cell walls. Not only is chitosan inexpensive and abundant, it is a strong adsorbent for heavy metals (Berkeley, 1979; Yang and Zall, 1984). Our results showed that chitosan was very effective in fresh and salt water at sorbing Cd, Co, Cu, Ni, Pb, and Zn (Figure 2). Mixing it with North Carolina apatite increased its effectiveness for As and Se (Figure 2). Other researchers also reported high adsorption capacities of chitosan for Cd, Cr, Hg, and Pb (Yang and Zall, 1984).

A sand treatment served as a control treatment in all experiments. The sand was collected at the Savannah River Site, Aiken, SC, and was not pure; for example, it had 0.6% of organic matter. Using this sand enhanced realism because quarried sand would be expected to have a small amount of clay or organic matter. Sorption of all metals on the sand was near zero in fresh and salt water (Figure 2).

Retention of metals by the amendments was evaluated in a series of experiments, in which the residue from the removal (sorption) studies was extracted with 1 M  $\text{MgCl}_2$  solution, which is commonly used to determine the bioavailable and mobile pool of metals (Tessier et al., 1979). The retention studies determined how strongly metals were bound to the amendments in fresh and salt water. Scientific understanding of binding strength and the irreversibility of reactions is essential to obtain regulator approval of in - situ immobilization as an acceptable remediation strategy because these variables have a direct effect on bioavailability and mobility. Although amendments remove contaminants from water very efficiently, subsequent contaminant remobilization from the amendments can release contaminants back to the water or treated sediments. The manner in which an amendment desorbs contaminants depends on its binding capacity and retention. Choosing the most appropriate treatment requires an understanding of how amendments bind contaminants and the conditions under which they could release the removed metals back into the water column.



**FIGURE 2.** Comparison of removal of As, Cd, Cr, Co, Cu, Ni, Pb, Se, and Zn in fresh and salt water (concentration of each metal in the spike solution was  $\sim 1 \text{ mg L}^{-1}$ ).

Tables 1 and 2 show retention in fresh and salt water. Retention was calculating following equation number 2. Almost all tested amendments showed high retention (80% or more) for Cr, Cu, Pb, and Zn (Table 1 and 2). The best Cd retention was for organoclay (OCB-750), chitosan, and the mixture of North Carolina apatite and chitosan (Table 1). The highest retention (80% or more) of As was by organoclay (OCB-750) and aquablock with

**TABLE 1.** Evaluation of amendment effectiveness in fresh water based on retention of metals<sup>a</sup> (acronyms as in Figure 1).

Amendment	As	Cd	Co	Cr	Cu	Ni	Pb	Se	Zn
RPT	X		XX	XX	XXX	X	XXX		X
NCA	X		XX	XXX	XXX	XX	XXX	XXX	XX
CaP			XX	XXX	XXX	XX	XXX		XXX
OCB-750	XXX	XXX	XXX	XXX	XXX	XXX	XXX		XXX
AB 8			XX	XX	XXX	XX	XX		XX
AB-ZVI	XXX		XX	XX	XXX	XX	XX		XX
ZC			X	XXX	XX		XXX		X
BPC		XXX	XXX	XX	XXX	XXX	XXX		XX
NCA/BPC50%	X	XXX	XXX	XXX	XXX	XXX	XXX	XX	XXX

<sup>a</sup> X - retention at 30 - 50%; XX - retention at 50 - 80%; XXX - retention at 80 - 100%

**TABLE 2.** Evaluation of amendment effectiveness in salt water based on retention of metals<sup>a</sup> (acronyms as in Figure 1).

Amendment	As	Cd	Cr	Co	Cu	Ni	Pb	Se	Zn
RPT	XX		XX	XX	XXX	XX	XXX		XXX
NCA	X		XX		XX		XXX	XX	XX
CaP		X	XX		XXX		XXX		XXX
OCB-750	XXX	XXX	XX	XXX	XXX	XXX	XXX	XX	XX
AB*	X		XX	X	XXX	X	XX		XXX
AB-ZVI	XXX		XX	XX	XXX	XX	XXX	XX	XX
ZC			XX		XX		XXX		XX
BPC		XXX		XXX	XXX	XXX	XX		XXX
NCA/BPC50%		XXX		XXX	XX	XXX	XXX	XX	XXX

<sup>a</sup> X - retention at 30 - 50%; XX - retention at 50 - 80%; XXX - retention at 80 - 100%

zero valent iron coating (AB-ZVI) (Table 1). In fresh water only NC apatite and the mixture of NC apatite and chitosan had Se retention higher than 50% (Table 1). Retention in fresh and salt water was similar for Cu, Cr, Ni, Pb, and Zn, mostly 80% or higher (Table 1 and 2).

## CONCLUSIONS

Laboratory batch studies showed that phosphates amendments, some organoclays, and the biopolymer, chitosan, are very effective in removing metals from both fresh and salt water. They also showed that all amendments exhibited high retention (80% or more) of Cr, Cu, Pb, and Zn in fresh and salt water suggesting reduced potential for remobilization of these metals. Selenium retention was greatest for NC apatite and the mixture of NC apatite and chitosan. The amendments are now being evaluated further as components in the development of active caps for sediment remediation.



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